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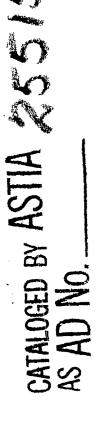*Reproduced*
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RATES OF EVAPORATION OF LIQUIDS

by

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ABSTRACT

The rate of evaporation of a pure liquid at temperature T into a vacuum is shown to be equal to $\alpha \cdot c \cdot n_s$ where α is a coefficient depending on equilibrium molecular properties, c is one-fourth the gas-kinetic mean velocity of the molecules at temperature T and n_s is the number density of the vapor molecules in equilibrium with the liquid at T.

This result is not new. Its derivation and underlying assumptions are of considerable theoretical interest. Previous derivations which have led to similar or slightly different results are discussed.

Introduction

In 1882, from gas kinetic theory, Hertz (1) arrived at the conclusion that there must exist a maximum rate of evaporation r_e from a liquid surface at a temperature T into a vacuum. According to Hertz:

$$r_e = \bar{c} \cdot n_s \tag{1}$$

where $\bar{c}$ is one-fourth the gas-kinetic mean molecular speed at temperature T and n_s is the number density of molecules of vapor in equilibrium with the liquid at T.

This result of Hertz is of special interest in that it showed for the first time how a rate process could be calculated from gas kinetic theory supplemented by a fundamental assumption of equilibrium.

Indeed, the reasoning behind equation (1) is as follows. Consider a liquid in equilibrium with its vapor. From gas-kinetic theory, the frequency of collisions of vapor molecules with the surface is given by $c \cdot n_s$. If every collision leads to condensation, $c \cdot n_s$ represents also the rate of condensation and it is the maximum rate of condensation. Since equilibrium prevails, $c \cdot n_s$ is also the maximum rate of evaporation. If now all molecules in the vapor phase are removed so that the liquid is allowed to evaporate freely into a vacuum, it is assumed that the maximum rate of evaporation is still given by the equilibrium value $c \cdot n_s$.

If, on the other hand, as first noted by Knudsen (2), only a fraction α of the molecules striking the surface at equilibrium actually condenses, the maximum rate of condensation and evaporation at equilibrium is $\alpha \cdot c \cdot n_s$. Again, if it is assumed that the same rate obtains away from equilibrium, the maximum rate of evaporation into a vacuum becomes:

$$r_e = \alpha \cdot c \cdot n_s \tag{2}$$

where α is the so-called evaporation or condensation coefficient. It is clear that α must have the same value for condensation and evaporation since it was first introduced to describe an equilibrium process. Then by virtue of microscopic reversibility, α must be the same in both directions. On the other hand, if evaporation ceased to be an equilibrium process away from equilibrium, the value of α might very well change and be different for condensation or evaporation.

The expression of Hertz as modified by Knudsen was first verified by the latter in a study of the evaporation of mercury. Knudsen (2) found $\alpha = 1$ for mercury. This result was confirmed by Volmer and Estermann (3) who found $\alpha = 1.00 \pm 0.07$ for mercury in an extended temperature range where the rate of evaporation varied by a factor of more than 10^3.

Thus, the theoretical result of Hertz rests on solid experimental grounds. There still exists no other case where a

rate process has been calculated and the calculated value submitted to such a close experimental verification. In particular, the fundamental assumption of equilibrium must be considered as proved by the careful data of Volmer and Estermann.

In the case of molecules with internal degrees of freedom, gas-kinetic theory may be inadequate and it is of interest to apply absolute rate theory to the problem of evaporation. The importance of rotational motion in this problem was first pointed out by Herzfeld (4). In what follows, the rate of evaporation will be derived from the usual form of absolute rate theory. This derivation will then be compared to other derivations in the literature.

Rate of Evaporation at Equilibrium

The simplest approach is to repeat the reasoning of Hertz. If, at first, the molecule considered has no internal degrees of freedom, the result of Hertz must of course be reproduced.

In a system containing liquid and vapor in equilibrium, the rate of condensation r_c will be given by the usual formula of absolute rate theory:

$$r_c = \nu \ \frac{F^{\ddagger}}{F_g} \ n_s \cdot e^{-\frac{E_o^{\ddagger}}{RT}} \tag{3}$$

Notations are as follows:

ν : Eyring's frequency : kT/h

$F^{\ddagger}$: the partition function of the transition state per unit interfacial area

F_g : the partition function of the gas molecules per unit volume

$E_o^{\ddagger}$: the activation energy at absolute zero.

The transmission coefficient has been assumed to be equal to unity. If there is no activation barrier, (3) reduces to:

$$r_c = \nu \ \frac{F^{\ddagger}}{F_g} \ n_s \tag{4}$$

The assumption will now be made that the transition state still possesses translational mobility in two dimensions, parallel to the surface. Since the molecules have no internal degrees of freedom, both $F^{\ddagger}$ and F_g have translational contributions only, respectively in two and three dimensions. Therefore:

$$F^{\ddagger} = (\nu/c)^2 \tag{5}$$

$$F_g = (\nu/c)^2 \tag{6}$$

Substitution of (5) and (6) into (4) gives:

$$r_c = \ddot{c} \cdot n_s$$

But since the liquid is in equilibrium with the vapor, $r_c = r_e$. If, as in the classical theory, it is now assumed that this is also the rate of evaporation when all molecules in the vapor are removed:

$$r_e = c \cdot n_s$$

an expression identical to (1) as expected. The case of interest
is that where the molecules have internal motion characterized
in the gas and in the transition state by the internal partition
functions f_g and $f^{\ddagger}$ respectively.

Then:

$$F^{\ddagger} = (v/c)^2 \, f^{\ddagger} \tag{7}$$

$$F_g = (v/c)^3 \, f_g \tag{8}$$

Hence, the rate of evaporation becomes:

$$r_e = (f^{\ddagger}/f_g) \cdot c \cdot n_s \tag{9}$$

A final assumption is to take for the internal partition
function of the transition state the value of the internal parti-
tion function of the liquid, f_L.

The result is now:

$$r_e = (f_L/f_g) \, c \cdot n_s \tag{10}$$

It is tempting to identify f_L/f_g with the evaporation
coefficient α :

$$\alpha = \frac{f_L}{f_g} \tag{11}$$

Calculation of α is then feasible in principle from
equilibrium properties of the liquid and its vapor.

Rate of Evaporation into a Vacuum

The same result should be obtained without recourse to the circuitous route imagined by Hertz. But then it is necessary to use a particular model of the liquid although the details of this model must disappear in the final expression for the rate of evaporation.

Following essentially the reasoning of Penner (5), the calculation of the rate will be done on the basis of the free volume theory of Kinkaid and Eyring (6).

First, the relation between free volume, saturation pressure and heat of vaporization will be recalled. Then this result will be applied to the calculation of the rate of evaporation.

The complete partition function Q_L for one mole (N molecules) of the liquid is:

$$Q_L = \frac{1}{N!} \left\{ (\nu/c)^3 \, V_f \, \exp \, (E/RT) \cdot f_L \right\}^N \qquad (12)$$

where V_f is the free volume of the liquid, per mole and E is the molar internal energy of vaporization at absolute zero.

On the other hand, the complete partition function for one mole of ideal vapor occupying a volume V is:

$$Q_g = \frac{1}{N!} \left\{ (\nu/c)^3 \, V \cdot f_g \right\}^N \qquad (13)$$

The Helmoltz free energy F per mole is related to the complete partition function Q :

$$F = -kT \ln Q \qquad (14)$$

The molar Gibbs free energy or chemical potential μ of liquid and vapor are then given by the expressions:

$$\mu_L = -kT \ln Q_L + p V_L = -kT \ln Q_L \qquad (15)$$

$$\mu_g = -kT \ln Q_g + p V = -kT \ln Q_g + RT \qquad (16)$$

since the term $p V_L$ for a condensed phase can be neglected.

At equilibrium between liquid and vapor $\mu_L = \mu_g$, or :

$$\ln \frac{V_f \cdot f_L \cdot \exp(E/RT)}{V \cdot f_g} = -1 \qquad (17)$$

Therefore, putting as before $(f_L/f_g) = \alpha$:

$$\alpha \cdot \frac{V_f}{V} = e^{-1} \cdot e^{-E/RT} \qquad (18)$$

Introducing volumes per molecule $v = V/N$ and $v_f = V_f/N$ and noting that $v = (1/n_s)$, we have finally:

$$v_f = \frac{1}{\alpha \cdot e \cdot n_s} e^{-E/RT} \qquad (19)$$

To calculate the rate of evaporation, the following usual assumptions are now made: the transition state is in equilibrium with reactants and the transmission coefficient is unity. Then:

$$r_e = v \cdot n^{\ddagger} \qquad (20)$$

where $n^{\ddagger}$ is the number of activated complexes per unit inter-facial area. The activated complex is assumed, as previously, to

be free to translate in two dimensions parallel to the surface. In the calculation of $n^{\ddagger}$, the translation along the reaction coordinate must be omitted. Finally, the internal partition function of the activated complex is assumed to be identical to that in the liquid.

Then the complete partition function $Q^{\ddagger}$ for the transition state is:

$$Q^{\ddagger} = \left\{ (\nu/c)^2 \cdot f_L \cdot a \right\}^N \tag{21}$$

where a is the area available to each activated complex and therefore $a = 1/n^{\ddagger}$. The equilibrium condition:

$$\mu_L = \mu^{\ddagger}$$

where $\mu^{\ddagger}$ is the chemical potential of activated complexes gives now:

$$\ell n \frac{(\nu/c) \ V_f \cdot \exp \ (E/RT)}{(N!)^{1/N} \ a} = 0 \tag{22}$$

Hence:

$$(\nu/c) \ \frac{V_f}{a} = e^{-1} \ e^{-E/RT} \tag{23}$$

since by Stirling's approximation:

$$N! = (N/e)^N \tag{24}$$

Thus:

$$n^{\ddagger} = \frac{1}{V_f \cdot (\nu/c) \cdot e} \ e^{-E/RT} \tag{25}$$

Finally:

$$r_e = \nu \cdot n^{\ddagger} = \frac{c}{e \cdot v_f} \; e^{-E/RT} \tag{26}$$

The free volume per molecule in the liquid can now be eliminated by substitution of its value derived above (19):

$$r_e = \frac{c}{e} \; e^{-E/RT} \cdot \frac{\alpha \cdot e \cdot n_s}{e^{-E/RT}} \tag{27}$$

As expected, the result is identical to that obtained previously (10):

$$r_e = \alpha \cdot c \cdot n_s \tag{28}$$

Discussion

In the final result, equation (28), any reference to the particular model of the liquid has disappeared and the expression for the rate of evaporation is the same as equation (10) which was derived following the method of Hertz without any assumption as to the nature of the liquid state.

If a different assumption is made concerning the modes of motion of the liquid, the final result, equation (28) will not be affected because its derivation rests on the two equilibrium relations:

$$\mu_L = \mu^{\ddagger}$$

$$\mu_L = \mu_g$$

between which the value of the free volume is eliminated.

For example, in the treatment just given, it has been assumed implicitly that the liquid possessed its full communal entropy. Indeed, the partition function for the liquid given by equation (12) gives to each molecule the possibility of roaming through the total free volume V_f.

If it is now assumed, for instance, that each molecule is restricted to motion within its own cell, the communal entropy vanishes and (12) becomes:

$$Q_L' = \left\{ (v/c)^3 \, v_f \, \exp \, (E/RT) \cdot f_L \right\}^N \tag{12'}$$

Then the condition for equilibrium between liquid and vapor gives for the free volume per molecule a value e times larger than previously:

$$v_f = \frac{1}{\alpha \cdot n_s} \, e^{-E/RT} \tag{19'}$$

But, correspondingly, the condition for equilibrium between liquid and transition state will lead to a value for $n^{\ddagger}$ which is also e times larger than previously:

$$n^{\ddagger} = \frac{1}{v_f \, (v/c) \cdot} \, e^{-E/RT} \tag{25'}$$

so that the final result (28) is the same as before. However, Penner in his original derivation (5) used essentially equation (25') together with equation (19): this led him to a value for r_e:

$$r_e = e \cdot \alpha \cdot c \cdot n_s$$

which is of course e times too high. He then speculated that this value should be reduced by a transmission coefficient smaller than unity, expressing the possible failure of the equilibrium hypothesis. The situation has been clarified (7) and it is now clear that the correct expression (28) can be obtained without recourse to any ad hoc assumption concerning the fundamental equilibrium hypothesis or the transmission coefficient.

More recently, Mortensen and Eyring have derived once more equation (28): their method is somewhat confusing in our opinion because they identify $\alpha = f_L/f_G$ with the transmission coefficient in the customary rate equation. This, of course, is not necessary at all. In particular, as shown above, evaporation can be treated like a perfectly normal rate process with a transmission coefficient equal to unity and the usual equilibrium between activated state and reactants.

Since α can be evaluated in several ways, as shown by Mortensen and Eyring (8), it becomes highly interesting, from the standpoint of theoretical chemical kinetics, to accumulate reliable experimental data on the rate of evaporation of liquids.

This has been undertaken in our Laboratory and results obtained with glycerol have been discussed elsewhere (9). Further work is now in progress, using other associated liquids for which values of α smaller than unity are expected theoretically. The possibility, in such studies, of throwing more light on the nature of the transition state, appears quite attractive.

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